TERTIARY AMINE BISULFITES

BY

ROBERT DEWALD LIPSCOMB

B.S., The University of Nebraska, 1940
M.S., The University of Illinois, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1944

URBANA, ILLINOIS
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Introduction

The reaction of alkali metal bisulfites with aldehydes and certain ketones to form addition compounds has long been known. The present investigation was designed to determine if a basic organic residue can replace the alkali metal in the addition compounds and to observe the properties of the addition compounds. By producing in this manner a molecule that is no longer a metallo-organic type of compound, the scope of the reaction might be extended.

Discussion

Tertiary amines of sufficient basicity were found to react with sulfur dioxide, in the presence of water, to form amine bisulfites. These compounds were yellow or orange colored, slightly viscous liquids of moderate stability. Excess sulfur dioxide was always found to be present in the orange liquids, possibly combined as a loose molecular compound. It was evolved slowly when the bisulfites were allowed to stand in air at room temperature or more rapidly when they were caused to react with carbonyl compounds.

Bisulfites were prepared from trimethylamine, N-methylpiperidine, N-*n*-butylpiperidine, N-*n*-butylmorpholine, N-*n*-benzylpiperidine, N-*n*-benzylmorpholine, N-laurylpiperdine, N-cetylpiperidine, and pyridine. Characteristic of most salts, they were soluble in water and nearly insoluble in ether.

The reaction between tertiary amine bisulfites and aldehydes or ketones was observed to take place. When the two reactants were mixed, heat and sulfur dioxide were evolved and decolorization and crystallization took place. The addition products were all white, crystalline solids, easily purified by recrystallization from alcohol or alcohol-ether mixtures. Analyses indicate that they have the composition of an addition product consisting of one mole of amine bisulfite with one mole of the carbonyl compound. By analogy to the reaction between the alkali metal bisulfites and carbonyl compounds, the products are very probably of the α-hydroxysulfonate type.

All of the bisulfites were allowed to react with one or more of the following carbonyl compounds: benzaldehyde, acetone, methyl n-propyl ketone, cyclohexanone, cyclopentanone, and 2-ethylhexanal. The addition compounds, like those of alkali metal bisulfites, were only moderately stable and were easily decomposed by dilute mineral acids and alkalis, but unlike the alkali metal bisulfite addition compounds, possessed sharp melting points. This property may lend itself to the identification of aldehydes and ketones by means of the amine bisulfites.

Vita

The writer was born in Tulia, Texas on December 29, 1917. He received his elementary education in the public schools of Wymore, Nebraska and Nebraska City, Nebraska. He was graduated from Nebraska City High School in May, 1935. In September, 1936, he entered the University of Nebraska from which he received the degree of Bachelor of Science in February, 1940, and the degree of Master of Science in August, 1941. In the fall of 1941 he enrolled in the graduate school of the University of Illinois, where he held the position of special research assistant during the academic years 1941-2, 1942-3, and 1943-4 except during the period from September, 1942, through November, 1942, when he held the General Aniline and Film Corporation Fellowship.

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